

Dielectric Relaxation Spectroscopy

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Introduction

Dielectric Relaxation Spectroscopy (DRS) probes the interaction of a macroscopic sample with a time-dependent electric field. The resulting polarization, either expressed by the frequency-dependent complex permittivity and conductivity or as an impedance spectrum, characterizes amplitude and timescale (via the relaxation time) of the charge-density fluctuations within the sample. Such fluctuations generally arise from the reorientation of the permanent dipole moments of individual molecules or from the rotation of dipolar moieties in flexible molecules, like polymers. Other possible mechanisms include the transport of ions or the appearance of interfacial charges in heterogeneous systems. The timescale of these fluctuations depends on the sample and on the relevant relaxation mechanism. Relaxation times range from several picoseconds in low-viscosity liquids to hours in glasses, probably marking DRS as the technique with the most extensive coverage of dynamical processes. The corresponding measurement frequencies range from 10^{-4} Hz to 10^{12} Hz, which requires a series instruments for complete coverage. However, it is generally sufficient to concentrate on a smaller frequency range adapted to the sample properties. In contrast to conventional spectroscopic methods, like NMR or vibrational spectroscopy, DRS is especially sensitive to intermolecular interactions. DRS is able to monitor cooperative processes and thus provides a link between molecular spectroscopy, which monitors the properties of the individual constituents, and techniques characterizing the bulk properties of the sample, especially the viscoelastic and rheological behaviour. The deconvolution of the dielectric spectrum into its individual relaxation processes informs on the relative amplitudes and characteristic times of the underlying molecular motions.

DRS is widely applied in the characterization of ion-conducting solids, polymers and mesophases [1-3]. But it is also of large potential interest for the investigations of liquid systems [4-7]. Possible applications include:
Static permittivity [4-7]

The static permittivity, ϵ_0 , is a central solvent property which determines and reflects the magnitude of solute-solvent interactions. ϵ_0 influences the solubility of solutes, the formation of micelles or the osmotic coefficients of electrolytes. *Vice versa* ϵ_0 strongly depends on the composition of the solution (e.g. the static permittivity of pure N-methylformamide at 25°C is 184, but for a 0.5 *m* NaCl solution $\epsilon_0 = 111$ is observed). Note that DRS is the only technique which allows the determination of the static permittivity of electrically conducting liquids, like electrolyte solutions.

Dielectric heating [8]

DRS routinely determines the dielectric loss, ϵ'' , or $\tan \delta$ for samples of conductivity σ - the total loss, $\epsilon'' = \sigma / (2\pi\nu\epsilon_0)$, as a function of the frequency, ν ; ϵ_0 is the permittivity of the vacuum. These quantities characterize the absorption of electromagnetic energy by the sample and therefore determine the efficiency of dielectric heating (e.g. in microwave ovens).

Speciation in Electrolyte Solutions [7]

In electrolyte solutions ion-ion interactions may lead to the formation of aggregates, like ion-pairs or ion-triples. The identification and quantitative determination of such species is of crucial importance for the understanding of electrolyte properties and the modeling of geological and industrial processes. DRS is specific for species with a permanent dipole moment, like ion-pairs. In contrast to other spectroscopic techniques, which monitor only contact ion-pairs, DRS is also able to detect solvent-separated ion-pairs.

Dynamics of complex liquids - microheterogeneities, hydrophobic hydration [6,7]

DRS is especially sensitive to cooperative processes. For instance in the case of acetonitrile-water mixtures at $0.5 \leq x_{AN} \leq 0.8$, DRS data suggest the formation of micro-heterogeneous clusters of highly frustrated water in a matrix of nearly unperturbed acetonitrile. Around the hydrophobic tetraalkylammonium ions a shell of water molecules with strongly reduced mobility can be distinguished from bulk water.

DRS thus allows to monitor the influence of solute-solvent interactions on structure and dynamics of the *solvent* as well as of the *solute*. Such information is important for the understanding of solubilization phenomena.

Emulsions and microemulsions [4]

DRS yields information on the type of emulsion (o/w or w/o), emulsion stability and aggregation behaviour, droplet size and distribution.

The dynamics of stabilizers and additives, as well as their interaction with water can be investigated.

Colloids [4]

DRS monitors counterion diffusion on the surface of colloidal particles. From the observed relaxation time information on particle size and shape can be inferred.

Micelles and liposomes [4]

DRS yields information on the particle size and allows the determination of the phase diagram.

From the individual spectral contributions specific information on the headgroup dynamics of the surfactant molecules as well as on the structure of the hydration shell can be obtained. Additionally, the interactions of polar probe molecules with the different environments present in such systems can be investigated.

Due to its high sensitivity towards conducting contaminants, DRS is very effective in the purity control of liposomes.

The timescales covered by these solution processes range from milli- to picoseconds, so that experiments must be conducted in the range of radio- to microwaves. Due to now available impedance analyzers dielectric relaxation studies up to 3 GHz are becoming increasingly popular for the investigation of complex liquids, see ref.[4]. However, a perusal of the literature reveals that generally the interpretation of the data is not as unambiguous as one would wish. This essentially arises from the large bandwidths of the spectral components, so that precise spectra over a broad frequency range are necessary for a meaningful deconvolution. Since commercial instruments cannot cover the relaxation range of the solvent appropriately (e.g. water peaks at 20 GHz - already in a frequency range difficult to access), such limited investigations do not only forbid a characterization of the *solvent response*, but also hamper a precise separation of the *solute contribution* or of specific cooperative relaxation processes (e.g. of micelles, emulsions, colloids).

Coming from the investigation of "simple" liquids and solutions with experience in the development of DRS instrumentation for highly conducting electrolyte solutions, our laboratory is now able to perform DRS experiments in the frequency range $0.001 \leq \nu / \text{GHz} \leq 89$ with 2% accuracy relative to ϵ'' . We are unique in being able to cover both *solute* and *solvent* response with high accuracy for temperatures between -45°C and 65°C [5,7].

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 [5] R.Buchner and J.Barthel, *Dielectric Relaxation in Solutions*, Annu. Rep. Prog. Chem., Sect. C, **91** (1994) 71-106;
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 [6] U.Kaatze, *The Dielectric Properties of Water in Its Different States of Interaction*, J. Solution Chem. **26** (1997) 1049-1112.
 [7] J.Barthel et al., *Dielectric Relaxation Spectroscopy of Electrolyte Solutions. Recent Developments and Prospects*, J. Mol. Liq. **78** (1998) 82-109.
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Facilities Instrumentation

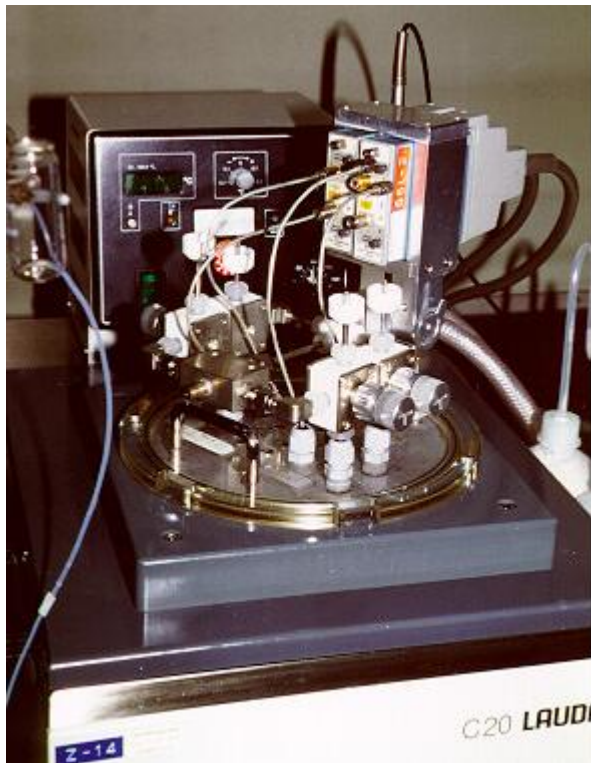
In our laboratory we are currently able to cover the frequency range $0.001 \leq \nu / \text{GHz} \leq 89$ with an accuracy of 2% in ϵ'' and $\epsilon'' = \epsilon''_0 + \nu / (2\pi\sigma_0)$ relative to the static permittivity of the sample.

The DRS equipment is optimized for samples of high polarity and/or high electric conductivity. It was successfully used to investigate liquid samples with static permittivities $6 \leq \epsilon' \leq 300$, conductivities up to 12.5 S/m and viscosities up to 1 Pa-s.

The instrumentation, developed in Regensburg, consists of a Time-Domain Reflectometer (TDR)

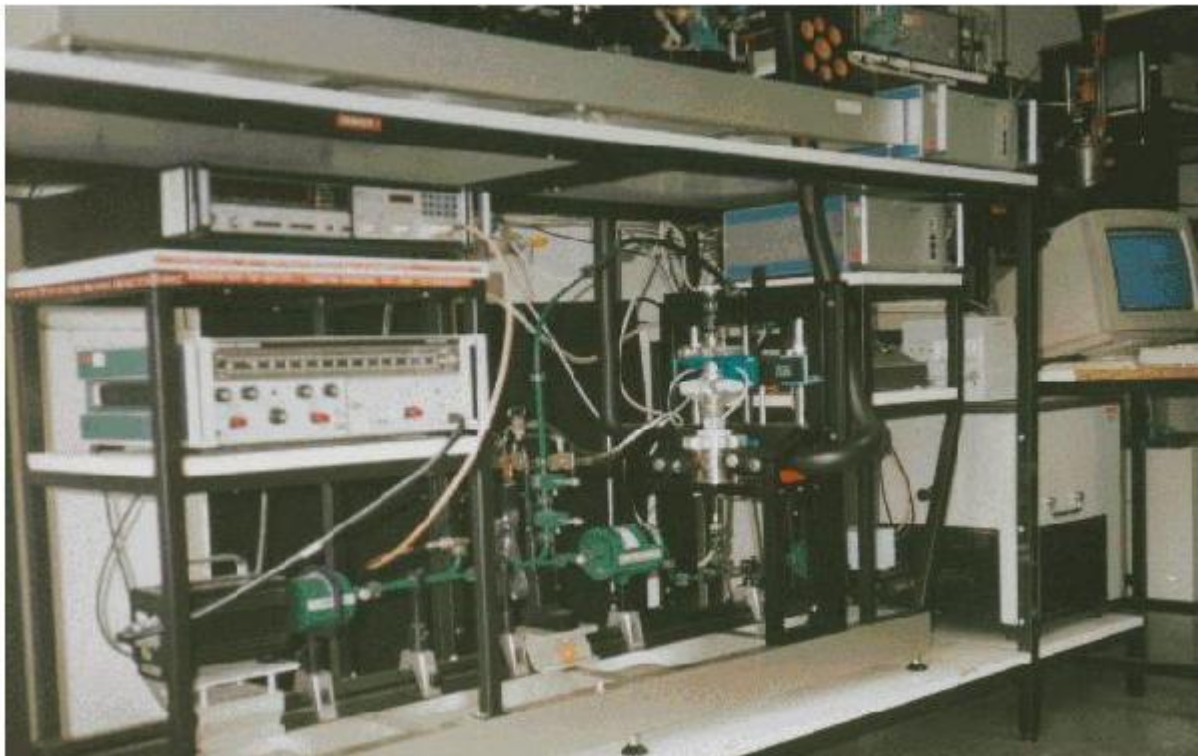
for $0.001 \leq \nu / \text{GHz} \leq 10$ at temperatures $-45 \leq T / ^\circ\text{C} \leq 65$ with a series of cells optimized

for different permittivity and frequency ranges



wave-guide interferometers with variable path-length cells for

- X-band ($8.5 \leq f / \text{GHz} \leq 12.4$) at $15 \leq T / ^\circ\text{C} \leq 30$
- Ku-band ($12.4 \leq f / \text{GHz} \leq 18$) at $-25 \leq T / ^\circ\text{C} \leq 65$
- Ka-band ($26.5 \leq f / \text{GHz} \leq 40$) at $-25 \leq T / ^\circ\text{C} \leq 65$
- X-band ($60 \leq f / \text{GHz} \leq 90$) at $-25 \leq T / ^\circ\text{C} \leq 65$



Auxiliary Data

Measurements of auxiliary data required for the analysis of the complex permittivity spectra (conductivity, density, viscosity) are performed in the same laboratory.

Data analysis

For the deconvolution of the complex permittivity spectra into individual relaxation processes and the visualisation of the results a software package was developed which simultaneously fits the real and the imaginary parts of the complex permittivity.

Relaxation models with up to 10 relaxation processes may be defined. Currently the equations of *Debye*, *Cole-Cole*, *Davidson-Cole*, *Havriliak-Negami*, *Froehlich*, *Powles-Rocard*, and *Dissado-Hill* are implemented as possible band-shape functions for the individual processes. The quality of the fit can be judged by its variance.

Software: [Mwfit](#)

Projects

Dynamics and phase behaviour of ionic and non-ionic microemulsions

(S.Schrödle, P.Fernandez, R.Buchner,W.Kunz)

Dynamics of LiCl/dimethylacetamide - a solvent for cellulose

(S. Chrapava, W. Kunz, R. Buchner)

Is there pre-micellar aggregation in aqueous hexatrimethylammonium bromide solutions?

(N. Rohman, R. Buchner, W. Kunz)

Protein hydration

(D. Sarauli, D.E. Khoshtariya (Georgian Academy of Sciences, Tbilissi, Georgia), W. Kunz, R. Buchner)

Ion solvation and association in aqueous and non-aqueous solvents (R.Buchner, J.Barthel)

Hydration and ion association of divalent metal sulfates

(R.Buchner with Ting Chen,G.T.Hefter and P.M.May, Murdoch University, Australia)

Cooperative dynamics in alcohol-water mixtures

(T. Sato, Waseda University, Japan, and R. Buchner)

Inter- and intramolecular dynamics of Oligoethylene glycols (S. Schrödle, R.Buchner)

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see [Publications R. Buchner](#) and:

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